

## ETHOXYLATED POLYURETHANE VISCOSITY ENHANCERS

### FIELD OF THE INVENTION

The invention provides personal care products comprising fatty ethoxylated dimeric urethane compounds that enhance the viscosity of constituent water based surfactant systems. In compositions and methods of the invention, ethoxylated nonionic, urethane dimers increase the viscosity of personal care product water based surfactant systems and serve as thickeners. These thickeners produce clear solutions in combination with surfactants and can be made sufficiently water soluble to produce clear solutions in water. The thickeners are compatible with anionic, cationic, amphoteric and nonionic surfactants and are functional and stable over a wide pH range.

### BACKGROUND OF THE INVENTION

Viscosity control is necessary in personal care products to ensure stability, consistent dispensing, and desirable aesthetic properties. Personal care product viscosity can be controlled in many different ways. One common method uses water soluble polymers such as cellulose, acrylates, natural gums, ethoxylates and related derivatives. Ethoxylate thickeners typically comprise fatty acid esters of highly ethoxylated diols and polyols and include PEG 6000 distearate, a 150 mole ethoxylate formed by reaction of one mole of ethylene glycol, 150 moles of ethylene oxide and two moles of stearic acid. PEG 6000 distearate has been used as a viscosity building agent in a number of baby shampoos and has represented the standard in the industry. A 5% w/w concentration of PEG 6000 in water has a viscosity of about 1500 to 2000 cps. Such a solution in water becomes cloudy/pearlescent over time and viscosity is reasonably stable at neutral pH. PEG 6000 distearate forms a clear solution at 3% w/w concentration in 3% active sodium laurylether (2) sulfate (SLES2) and such a solution has a viscosity of about 25,000 cps. By way of comparison, water has a viscosity of about 1 to 2 cps and a 3% SLES2 solution also has a viscosity that is less than 5 cps.

Glucamate DOE 120 (Dow Chemical) can be used as a personal care product thickener. Glucamate DOE 120 comprises about 120 moles of ethoxylate formed by the esterification of one mole of (120 mole ethoxylated) methyl glucoside with two moles of oleic acid. When solubilized in water at a concentration of 5% w/w, a clear solution is

formed and the solution has a viscosity of less than 50 cps. A 3% w/w solution of Glucamate DOE 120 in 3% active SLES2 yields a clear solution that has a viscosity of less than 50 cps.

Crothix (Croda Inc.) can be used as a personal care product thickener and is a tetra stearate ester made from a one hundred fifty mole ethoxylate of pentaerythritol. This product is not readily water soluble and, when mixed with water at 5% w/w, produces a cloudy/opaque discontinuous mixture containing numerous hydrated, sticky gel particles. Upon standing, this mixture becomes discontinuous with a hazy, low viscosity, watery layer at the top of the container and a cloudy/opaque soft, sticky gel layer on the bottom. No viscosity measurement of this mixture could be made. A 3% w/w solution in 3% active SLES2 produces a clear solution with a viscosity of about 1400 cps.

A typical baby shampoo formulation may include, for example, a combination of ethoxylated sorbitan ester, amphoteric surfactant, anionic surfactant and PEG 6000 distearate to yield a baby shampoo which is non-irritating to children's eyes (essentially a No Tear Shampoo).

All of the aforementioned thickeners are esters and, as such, have limited stability in water due to hydrolysis of the ester group. When the ester is hydrolyzed, viscosity decreases and clarity diminishes. Hydrolysis is problematic if product pH is either extremely acidic or basic. Limited hydrolytic stability limits the use of ester type viscosity builders and such compositions cannot be used in certain personal care products.

Foaming is also a problem in formulations that contain sorbitan ester ethoxylate, PEG 6000 distearate, or amphoterics as thickeners. PEG 6000 distearate, when used in concentrations approaching about 1.5% by weight, can decrease the foam height as measured by Ross-Miles foam determination equipment.

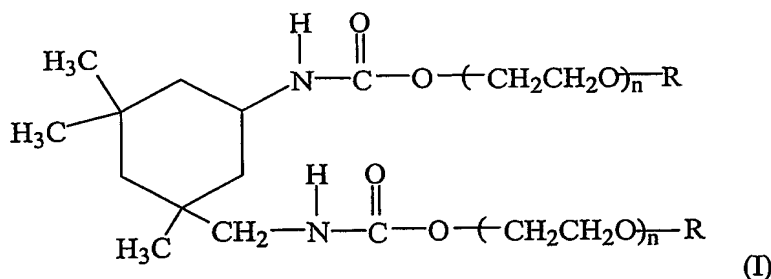
The need continues to exist, therefore, for thickeners that are useful in personal care products such as shampoos, that enhance the viscosity of constituent water based surfactant systems, and that are sufficiently water soluble to produce clear solutions in water. In particular, the need exists for personal care product thickeners that solubilize in the product and result in product viscosities preferably in the range of from about 5,000 to about 150,000 cps. Such thickeners should not depress foaming, should be stable over a wide pH range, and should be compatible with a broad range of surfactants.

### SUMMARY OF THE INVENTION

The invention provides personal care products comprising fatty ethoxylated dimeric urethane compounds that enhance the viscosity of constituent water based surfactant systems. In compositions and methods of the invention ethoxylated nonionic urethane dimers increase the viscosity of water based surfactant systems and serve as thickeners. These thickeners produce clear solutions in combination with surfactants and can be made sufficiently water soluble to produce clear solutions in water. While paint thickeners based on ethoxylated urethanes are known, the invention provides novel compositions and methods that use ethoxylated nonionic urethane dimers as thickeners in a broad array of personal care product applications.

The thickeners employed in the instant invention are compatible with anionic, cationic, amphoteric and nonionic surfactants and are functional and stable over a wide pH range. Thickeners used in the invention are long chain alcohol ethoxylated compounds in which the total ethoxylation ranges from about 100 to 240 moles of ethylene oxide, with a preferred amount of ethoxylation of approximately 130-140 moles, most preferably about 140 moles.

In particular in preferred aspects, the invention provides personal care products comprising fatty ethoxylated dimeric urethane compounds of the formula (I):



where n is a whole number from 50 to 120, preferably about 70 to 100, more preferably about 65-75, and most preferably about 70; and

R is a C<sub>12</sub>-C<sub>24</sub> (preferably, C<sub>15</sub>-C<sub>24</sub>) alkyl or alkenyl group.

Compounds of formula (I) can be made by reacting two moles of an ethoxylated fatty alcohol with a diisocyanate, most preferably isophorone diisocyanate.

When incorporated into personal care products such as lotions and shampoo formulations in accordance with the invention, compounds of formula (I) serve as thickeners and produce exceptional viscosity control. Compounds of formula (I): do not depress the foaming of shampoos; may be used to control and maintain the viscosity of personal care

products such as shampoos, hair conditioners, hair permanent waves, hair dyes, hair bleaches, hair relaxers, shaving products, skin cleansers, skin creams, skin lotions and soaps; exhibit thickening properties that are comparable or superior to other ethoxylated thickeners; are stable over a broad pH range (i.e., from a pH of less than about 1 to more than about 13, more particularly, from a pH of about 1 to about 13); and can be used in combination with anionic, cationic, amphoteric and nonionic surfactant systems. Solutions comprising thickeners of formula (I) solubilized in water and anionic, cationic, amphoteric, or nonionic surfactants, are substantially clear.

These and other aspects of the invention are disclosed further in the following detailed description.

#### DETAILED DESCRIPTION OF THE INVENTION

As used herein, the following terms have the following respective meanings. Other terms that are used to describe the present invention have the same definitions as those generally used by those skilled in the art. Specific examples recited in any definition are not intended to be limiting in any way.

"Alkyl" refers to a fully saturated monovalent hydrocarbon radical (containing 1 to about 24 carbon atoms) and hydrogen which may be a straight chain, branched, or cyclic. Examples of alkyl groups are methyl, ethyl, n-butyl, n-heptyl, isopropyl, 2-methylpropyl, cyclopropyl, cyclopropylmethyl, cyclobutyl, cyclopentyl, cyclopentylethyl and cyclohexyl as well as lauryl, myristyl, palmityl, stearyl and behenyl, among others. The term "alkyl" subsumes the term "alkylene" within context.

"Alkenyl" refers to a branched or unbranched hydrocarbon group typically although not necessarily containing from 2 to about 24 carbon atoms and at least one double bond, such as ethenyl, n-propenyl, isopropenyl, n-butenyl, isobutenyl, octenyl, decenyl, oleyl, linoleyl, linolenyl, erucyl and the like. Generally, although again not necessarily, alkenyl groups herein contain 12 to about 24, preferably 15 to about 24 carbon atoms.

The term "effective amount" is used throughout the specification to describe concentrations or amounts of compounds according to the present invention which are effective in conveying desired traits such as emulsification, clarification, adhesion, melting point modification or solubility to a formulation of a cosmetic, toiletry or personal care product.

The term "personal care product" is used throughout the specification to describe a cosmetic or toiletry product which is preferably used on or in contact with the hair, skin

and/or nails and which include effective concentrations of one or more of the compositions according to the present invention. Personal care products include, for example, cosmetics, floating bath oils, after shaves, creams, lotions, deodorants, including stick deodorants, pre-electric shave lotions, after-shave lotions, antiperspirants, shampoos, conditioners and rinses and related products, among others, including skin care products, eye makeups, body shampoos, protective skin formulations, lipsticks, lip glosses, after-bath splashes, presun and sun products, including sunscreens. Virtually any chemical product which comes into contact with the hair or skin and which may include effective amounts or concentrations of one or more of the compositions according to the present invention may be considered a personal care product according to the present invention. Personal care products according to the present invention comprise the dimeric urethane viscosity enhancer compositions, water and at least one additional component selected from the group consisting of surfactants/emulsifiers, solvents, coloring agents, secondary emulsifiers, humectants, emollients, moisturizing agents, pigments, anti-perspirant agents, aromatic or deodorizing agents, uv-absorbing compounds (for example, as used in sunscreens), preservatives, skin and/or hair conditioning agents, hair-straightening agents, solid organic polymers and waxes and mixtures thereof, among numerous others.

The term "stability" or "storage stability" shall mean stable (i.e., has an enduring quality which resists breaking down over time) at a temperature of no greater than about 50°C for a period of at least about three months, preferably at least about 6 months, more preferably at least about one year or more. The present compositions exhibit stability over a wide range of pH, a surprising characteristic.

The term "solvent" shall mean any cosmetically acceptable solvent, especially including, for example, ethanol, isopropanol, related alcohols, diols, such as propylene glycol, ethylene glycol, polyethylene glycol, among numerous others, where the inclusion of a solvent is applicable.

Ethoxylated fatty alcohol urethane dimers of formula (I) can be combined in personal care products in accordance with the invention with a variety of surfactant systems. Such surfactants include those that function as detergents to clean the hair. Conventional surfactants such as anionic, cationic and amphoteric surfactants can be used. In shampoo formulations, sodium-based surfactants are sometimes preferred over ammonium-based surfactants. Commercial sources of such surfactants can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1984, McCutcheon Division, MC Publishing Company, the complete disclosure of which is hereby incorporated

by reference. The amount of surfactant can range from about 1% to about 70% on a weight percentage basis, more typically from about 2% to about 50%. Preferred surfactants include ammonium lauryl sulfate, ammonium laureth sulfate, triethanolammonium lauryl sulfate, triethanolammonium laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauroyl sarcosine, cocoyl sarcosine, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, and cocoamphocarboxyglycinate. Ammonium laureth sulfate and sodium laureth sulfate are particularly preferred.

Ethoxylated fatty alcohol urethane dimers of formula (I) can be combined in personal care products in accordance with the invention with a variety of auxiliary conditioning agents such as quaternary ammonium compounds, amines, amine salts and other cationic polymers. Among the quaternary ammonium compounds which may be used are quaternary ammonium hydroxides, such as methyl triethanol ammonium hydroxide and tetraethyl ammonium hydroxide, among others. Preferred auxiliary conditioning agents include Stearalkonium chloride, Lapyrium chloride, steapyrium chloride, polyquaternium 10, polyquaternium 7, guar hydroxypropyltrimonium chloride or behentrimonium methosulfate. Such auxiliary conditioning agents can be used in an amount of from about 0.1% to about 3.0% on a weight percentage basis, preferably from about 0.5% to about 2.0%.

Ethoxylated fatty alcohol urethane dimers of formula (I) can be combined in personal care products in accordance with the invention with a variety of emollients including, but are not limited to, mineral oil, vegetable oils, cosmetic esters, silicone oils and petrolatum. Other emollients may include cetyl or stearyl alcohol, paraffin or lanolin alcohol. Emollients are generally employed in the formulations of the instant invention in a weight percentage range of from about 5% to about 45%, preferably from about 7.5% to about 40%.

Examples of suitable humectants include, but are not limited to, propylene glycol, hexylene glycol, glycerin and sorbitol. As a general guide, humectants are used in a weight percentage range of from about 1% to about 20%, preferably from about 4% to about 10%.

Ethoxylated fatty alcohol urethane dimers of formula (I) can be combined in personal care products in accordance with the invention with a variety of emulsifying agents. Emulsifiers typically provide dispersion and suspension of the components, and render a creamy and lubricous consistency to the composition. Nonlimiting examples of emulsifying agents suitable for use include alkoxylated alcohols and fatty alcohols, such as stearyl, cetyl

and cetearyl alcohols, ethoxylated sorbitan esters, ethoxylated lanolin and derivatives thereof. As a general guide, emulsifiers can be used in amounts of about 1% to about 16% on a weight percentage basis, preferably from about 2% to about 12%, and more preferably from about 8% to about 10%.

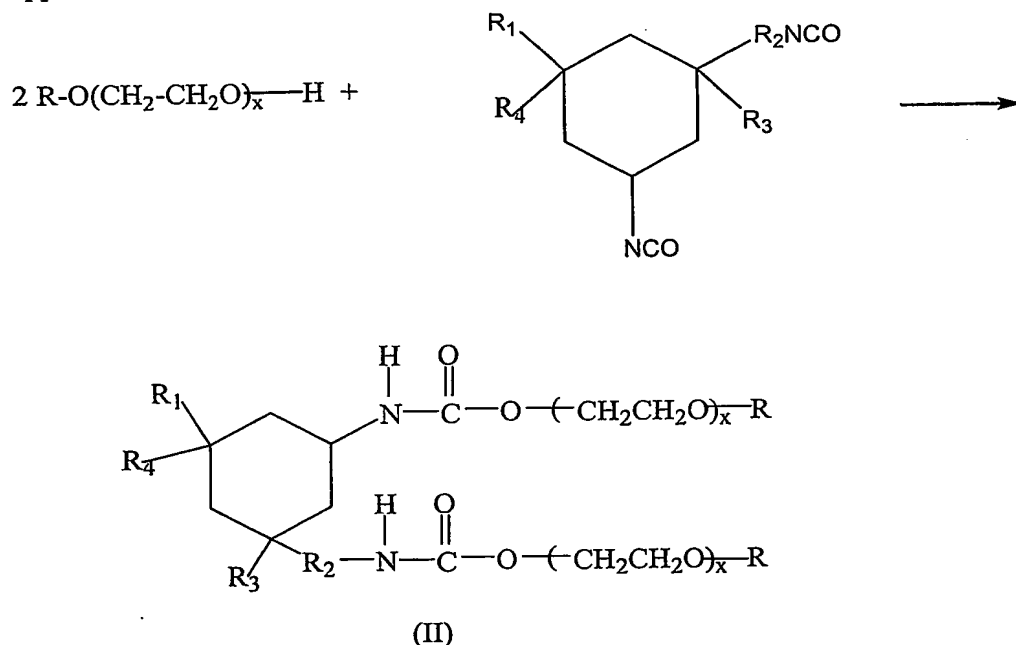
In the instant invention, ethoxylated fatty alcohol urethane dimers of formula (I) are included in personal care products/formulations in effective amounts, i.e., amounts which produce an intended effect. The amount of ethoxylated fatty alcohol urethane dimer of formula (I) generally is at least about 0.05% by weight and preferably ranges from about 0.5% to about 10% by weight or more of personal care formulations according to the present invention. In preferred embodiments, ethoxylated fatty alcohol urethane dimers of formula (I) are included in amounts ranging from about 0.5% to about 5% by weight. In preferred shampoos and conditioners, ethoxylated fatty alcohol urethane dimers of formula (I) are included in amounts ranging from about 1.0% to about 3% by weight of the formulation.

Ethoxylated fatty alcohol urethane dimers of formula (I) can be combined in personal care products in accordance with the invention with a variety of supplementary thickeners such as natural gums such as tragacanth, xanthan, acacia and locust bean, and synthetic gums such as hydroxypropylcellulose, hydroxyethyl cellulose and hydroxypropyl methylcellulose. Polyvinyl alcohols and Polyvinylpyrrolidone can also be used. Alkanolamides, "super" amides and the glycol or glycerol stearates may also be used.

Ethoxylated fatty alcohol urethane dimers of formula (I) can be combined in personal care products in accordance with the invention with other optional additives including antimicrobial preservatives, antioxidants such as sodium sulfite, chelating agents such as EDTA, suspending agents, fragrances or perfumes, herbal extracts and pH control agents such as citric acid. These additives are usually present in an amount of less than 5% on a weight percentage basis. Sunscreen agents maybe added in accordance with the FDA monograph regulations. In a shampoo, an antidandruff component, e.g., selenium sulfide, may also be included at an effective level.

Properties and characteristics of the ethoxylated fatty alcohol urethane dimers used in the present invention that make them especially useful as thickeners in personal care, cosmetic, and toiletry application include the following: extremely low order of toxicity and irritation; low color; excellent compatibility in cosmetic formulations; solubility with amides, sulfates, sulfonates sulfosuccinates, and sulfobetaines; nonrancidification; coupling characteristics; solubility in water, glycols and lower molecular weight alcohols; and excellent viscosity stability at extremes of pH.

As described, compounds of the present invention (which includes formula (I)) can be made by the reaction in the presence of heat and either an amine or tin catalyst such as stannous octanoate of an ethoxylated fatty alcohol with a diisocyanate, most preferably isophorone diisocyanate, in an approximately 2:1 molar ratio of ethoxylated fatty alcohol to isophorone diisocyanate, at a temperature of between about 80° C to about 120° C, at approximately atmospheric pressure, and in accordance with the following reaction scheme:



where x is a whole number from about 50 to 120; n is a whole number from 50 to 120, preferably about 70 to 100, more preferably about 65-70, and most preferably about 70; R is a C<sub>12</sub>-C<sub>24</sub> alkyl or alkenyl group; and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are the same or different and are a C<sub>1</sub> to C<sub>7</sub> alkyl or alkenyl group.

As the number of carbon atoms in the diisocyanate decreases, the number of carbon atoms in the monohydric alcohol may be increased accordingly to maintain similar chemical characteristics, provided the degree of ethoxylation of the ethoxylated fatty alcohol urethane dimers of formula (II) is maintained in the range specified hereinafter. In general, as the molecular weight of the ethoxylated fatty alcohol urethane dimers of formulas (I) or (II) increases as a consequence of the contribution from the non-ethoxylated portion of the molecule, the thickening properties of such compounds will increase. Conversely, if the ethoxylated portion of the molecule increases, the water solubility of the molecule may increase, resulting in a reduced thickening characteristic. Also, in general, as branching of



the ethoxylated fatty alcohol urethane dimers of formula (I) or (II) increases, thickening decreases.

Theoretically, the degree of ethoxylation can be any that is desired, but for purposes of building viscosity in cosmetic products such as skin creams and lotions and hair care products such as shampoos, conditioners and relaxers, fatty alcohols having from about 75 to about 150 moles of ethoxylation, more preferably from about 75 to about 100 moles of ethoxylation, are preferred. Urethane dimers of fatty alcohol ethoxylates with from about 100 moles of ethoxylation to 150 moles will typically make a clear solution in water with a viscosity of between 10,000 and 15,000 cps at 5% concentration.

Dimers made from fatty alcohols with lower degrees of ethoxylation (e.g., about 75 moles of ethoxylation) produce hazy/cloudy solutions in water and precipitate a water insoluble, sticky gel. However, when these poorly water soluble dimers are solubilized with an added surfactant, the resulting solution can exhibit a significantly higher viscosity as compared to a more ethoxylated, water soluble dimer.

Preferred fatty alcohols useful in making urethane dimers of fatty alcohol ethoxylates range from myristyl to behenyl alcohol ( $C_{14}$  to  $C_{22}$ ) and are more preferably either cetyl or stearyl alcohols ( $C_{16}$  and  $C_{18}$ ) and mixtures thereof. Dimers made with a 75 mole ethoxylate (or, for example, 100 mole ethoxylate) of a fatty alcohol are marketed under the tradename Dermothix 75 (or Dermothix 100). These materials are somewhat comparable in performance to the thickener Crothix (Croda, Inc.) which has similar solubility characteristics. Direct viscosity measurements of Dermothix 75 and Crothix are not possible, as the compositions are not sufficiently water soluble (See Examples 1 & 2 hereinafter). However, these thickeners can be solubilized by the addition of surfactants to make clear, viscous fluids.

For example, a 3% w/w concentration of the 75 mole ethoxylated stearyl alcohol dimer in 3% active sodium laureth sulfate produces a clear solution with a viscosity of 24,000 cps (See Example 5 hereinbelow). By comparison, a 3% solution of Crothix in 3% active SLES2 produces a viscosity of 1,400 cps (See Example 6 hereinafter). Thus, the addition of a solubilizing surfactant helps to dissolve the urethane dimer of fatty alcohol ethoxylate, allowing it to function as desired. Examples 3, 4, 7 and 8 illustrate the thickening effects of the more water soluble thickeners Dermothix 100 and PEG 6000 Distearate.

These and other aspects of the invention are described further in the following examples, which are illustrative and in no way limiting.

EXAMPLE 1Materials and Methods

In performing the following syntheses and preparing the following final formulations, the reagents which are used are indicated in the specific examples. Solvents, where used, are preferably distilled prior to use. Sources of other materials are indicated in the appropriate experimental section. In most instances, although not in every instance, trademarked materials are available from Alzo International, Inc., Sayreville, N.J. Other materials are readily available from other chemical manufacturers and suppliers.

Shampoo formulations 1-8 were formulated using the ingredients disclosed in Tables 1-2 and viscosity of the formulations was measured using a Brookfield RVT viscometer. Viscosity measurements for formulations 1-8 are listed in Table 3. Formulations 3 and 7 contained the ethoxylated fatty alcohol urethane dimer Dermothix 100 as a thickener and evidenced exceptional viscosity and clarity.

Table 1

<u>Ingredients</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
Dermothix 75	5.0	-----	-----	-----
Crothix	-----	5.0	-----	-----
Dermothix 100	-----	-----	5.0	-----
PEG 6000 Distearate	-----	-----	-----	5.0
Water	94.0	94.0	94.0	94.0
Phenobact (antimicrobial)	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
	100.0	100.0	100.0	100.0

Table 2

<u>Ingredients</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
Dermothix 75	3.0	-----	-----	-----
Crothix	-----	3.0	-----	-----
Dermothix 100	-----	-----	3.0	-----
PEG 6000 Distearate	-----	-----	-----	3.0
Sodium Laureth(2) Sulfate (30% active)	10.0	10.0	10.0	10.0
Water	86.0	86.0	86.0	86.0
Phenobact	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
	100.0	100.0	100.0	100.0

Table 3		
Viscosity Results		
Formulation	Viscosity (cps)	comments
1	-----	Not soluble
2	-----	Not soluble
3	12,500	Clear liquid
4	1,600	Clear liquid
5	24,000	Clear liquid
6	1,400	Clear liquid
7	12,500	Clear liquid
8	25,500	Clear liquid

### EXAMPLE 2

The dimer urethane ethoxylates are also determined to function as thickeners when used in combination with cationic surfactants in hair conditioner formulations 9, 10, 11, 12 and 13 of Table 4. The PEG 6000 Distearate was especially effective as a thickener, possibly due to complexation between the stearalkonium chloride and free stearic acid that is residual from the esterification of the PEG 6000. Viscosity measurements for formulations 9-13 were determined as in Example 1 and are set forth in Table 5.

Table 4					
Ingredients	9	10	11	12	13
	%	%	%	%	%
Dermothix 75	3.0	-----	-----	-----	-----
Crothix	-----	3.0	-----	-----	-----
Dermothix 100	-----	-----	3.0	-----	-----
PEG 6000 Distearate	-----	-----	-----	3.0	-----
Glucamate DOE 120	-----	-----	-----	-----	3.0
Stearalkonium Chloride	3.0	3.0	3.0	3.0	3.0
Water	93.0	93.0	93.0	93.0	93.0
Phenobact	1.0	1.0	1.0	1.0	1.0
	100.0	100.0	100.0	100.0	100.0

Table 5		
Viscosity Results		
Example#	Viscosity (cps)	comments*
9	28,800	Clear Liquid
10	4,600	Clear liquid
11	65,600	Clear liquid
12	142,000	Hazy/cloudy liquid
13	5	Clear liquid

\* Samples were stored at 50°C for 24 hours, then at RT (22°C) for 6 hrs. Sample temperature was 22°C prior to viscosity measurement. Subsequently (overnight) the samples showed precipitates and crystallization.

### EXAMPLE 3

The dimer urethane ethoxylates were also determined to function as thickeners when used in combination with amphoteric surfactants in shampoo formulations 14, 15, 16, 17, and 18 illustrated in Table 6. The amphoteric surfactant used to make these formulations was Foamtaine CAB from Alzo International, Inc., which has the INCI name Cocamidopropyl Betaine. Viscosity values for formulations 14-18 were determined as in Example 1 and are listed in Table 7. The solubility of the thickener in the surfactant solution was determined to be critical to achieving a functional viscosity in the final formula. The more soluble the thickener is in the solution, the less viscosity it produces.

Table 6

Ingredients	14	15	16	17	18
	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
Dermothix 75	3.0	----	----	----	----
Crothix	----	3.0	----	----	----
Dermothix 100	----	----	3.0	----	----
PEG 6000 Distearate	----	----	----	3.0	----
Glucamate DOE 120	----	----	----	----	3.0
Foamtaine CAB (30% active)	10.0	10.0	10.0	10.0	10.0
Water	86.0	86.0	86.0	86.0	86.0
Phenobact	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
	100.0	100.0	100.0	100.0	100.0

Table 7  
Viscosity Results

<u>Example#</u>	<u>Viscosity (cps)</u>	<u>comments</u>
14	-----	Cloudy 2 phase gel - not soluble
15	-----	Cloudy 2 phase gel - not soluble
16	17,800	Clear liquid
17	5,400	Clear liquid
18	12.5	Clear liquid

### EXAMPLE 4

Solutions of ethoxylated nonionic surfactants can also be thickened using the dimer urethane ethoxylates, as evidenced by shampoo formulations 19-30 of Tables 8-10. The ethoxylated nonionic surfactant used in these examples was Hetoxol CA-20 (INCI name

Ceteth-20)(Global Seven, Inc.). Glucamate DOE 120 was not used in these studies as it had shown poor viscosity building effects in preliminary evaluations. Viscosity values for formulations 19-30 were determined as in Example 1 and are listed in Table 11.

Table 8

Ingredients	19	20	21	22
	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
Dermothix 75	1.0	----	----	----
Crothix	----	1.0	----	----
Dermothix 100	----	----	1.0	----
PEG 6000 Distearate	----	----	----	1.0
Ceteth-20	5.0	5.0	5.0	5.0
Water	93.0	93.0	93.0	93.0
Phenobact	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
	100.0	100.0	100.0	100.0

Table 9

Ingredients	23	24	25	26
	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
Dermothix 75	3.0	----	----	----
Crothix	----	3.0	----	----
Dermothix 100	----	----	3.0	----
PEG 6000 Distearate	----	----	----	3.0
Ceteth-20	5.0	5.0	5.0	5.0
Water	91.0	91.0	91.0	91.0
Phenobact	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
	100.0	100.0	100.0	100.0

Table 10

Ingredients	27	28	29	30
	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
Dermothix 75	5.0	----	----	----
Crothix	----	5.0	----	----
Dermothix 100	----	----	5.0	----
PEG 6000 Distearate	----	----	----	5.0
Ceteth-20	5.0	5.0	5.0	5.0
Water	89.0	89.0	89.0	89.0
Phenobact	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
	100.0	100.0	100.0	100.0

Table 11

Example#	Viscosity (cps)	Viscosity Results comments
19	100	Clear liquid - 1% Thickener
20	12.5	Clear liquid - "
21	12.5	Clear liquid - "
22	12.5	Hazy liquid - "
23	19,500	Clear liquid - 3% Thickener
24	3750	Clear liquid - "
25	20,000	Clear liquid - "
26	2,750	Hazy/cloudy liquid - "
27	125,000	Clear liquid - 5% Thickener
28	27,500	Clear liquid - "
29	85,000	Clear liquid - "
30	14,250	Hazy/cloudy liquid - "

As evidenced by the viscosity values of Table 11, the composition and amount of the thickener added directly affects the viscosity of the surfactant solution. The solubility of the thickener in the surfactant solution is critical to achieving a functional viscosity in the final formula. The more soluble the thickener is in the solution, the less viscosity it produces. The hazy/cloudiness seen in the PEG 6000 Distearate solutions is attributed to the presence of free fatty acids that were not completely solubilized by the nonionic.

#### EXAMPLE 5

The formulations prepared in this Example were used to test the thickeners at pH extremes (formulations 31 through 38, Tables 12 and 13). Viscosity values for formulations 31-38 were determined as in Example 1 and are listed in Table 14.

The results of the experiments in this Example show that the urethane dimer thickeners are effective and stable at both high and low pH values, while the ester type thickeners are not useful under such conditions.

Table 12

Ingredients	31	32	33	34
	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
Dermothix 75	3.0	----	----	----
Crothix	----	3.0	----	----
Dermothix 100	----	----	3.0	----
PEG 6000 Distearate	----	----	----	3.0
Ceteth-20	5.0	5.0	5.0	5.0

Hydrochloric acid (37%)	1.0	1.0	1.0	1.0
Water	90.0	90.0	90.0	90.0
Phenobact	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
	100.0	100.0	100.0	100.0
pH	1.13	1.15	1.18	1.15

Table 13

Ingredients	35	36	37	38
	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
Dermothix 75	3.0	----	----	----
Crothix	----	3.0	----	----
Dermothix 100	----	----	3.0	----
PEG 6000 Distearate	----	----	----	3.0
Ceteth-20	5.0	5.0	5.0	5.0
Sodium Hydroxide (50%)	0.8	0.8	0.8	0.8
Water	90.2	90.2	90.2	90.2
Phenobact	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
	100.0	100.0	100.0	100.0
pH	12.69	12.70	12.67	12.71

Table 14

Viscosity Results:	24 hr.	After 5 days	After 2 weeks
<u>Example#</u>	<u>Viscosity (cps)</u>	<u>Viscosity (cps)</u>	<u>Viscosity(cps)</u>
31	15,250	18,000	15,000
32	2,250	47.5	<10
33	17,000	20,200	17,000
34	1,400	10	<10
35	12,000	12,500	9,000
36	5	5	5
37	14,750	16,500	10,250
38	5	5	5

EXAMPLE 6

Shampoo formulations were made with various thickeners in accordance with the invention and were determined to have the compositions and properties set forth in Tables 15-17. Viscosity values were determined as in the experiment of Example 1.

Table 15

Ingredients	39	40	41	42
	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
Dermothix 75	1.0	----	----	----
Crothix	----	1.0	----	----
Dermothix 100	----	----	1.0	----
PEG 6000 Distearate	----	----	----	1.0
Sodium Laureth(2) Sulfate	30.0	30.0	30.0	30.0
Foamtaine CAB	10.0	10.0	10.0	10.0
Water	58.0	58.0	58.0	58.0
Phenobact	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
	100.0	100.0	100.0	100.0

Table 16

Ingredients	43	44	45	46	47
	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
Dermothix 75	2.0	----	----	----	----
Crothix	----	2.0	----	----	----
Dermothix 100	----	----	2.0	----	----
PEG 6000 Distearate	----	----	----	2.0	----
Sodium Laureth(2) Sulfate	30.0	30.0	30.0	30.0	30.0
Foamtaine CAB	10.0	10.0	10.0	10.0	10.0
Water	57.0	57.0	57.0	57.0	59.0
Phenobact	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
	100.0	100.0	100.0	100.0	100.0

Table 17

Viscosity Results: Formulation	Viscosity (cps)	Initial/Final Foam Volume (mls)*	Comments
39	15,000	500/450	Clear liquid
40	22,000	410/360	Clear liquid
41	2,200	375/325	Clear liquid
42	7,000	410/360	Clear liquid
43	85,000	420/370	Clear liquid
44	82,500	450/410	Clear liquid
45	27,500	390/340	Clear liquid
46	50,000	410/370	Clear liquid
47	25	410/360	Clear liquid



The results of the experiments of this Example show that in a typical shampoo formula, the thickeners are all effective at increasing viscosity, although to a varying degree, and they do not have a deleterious effect upon the foam volumes generated by the shampoo.

The foam test used was a modified "rotating cylinder" type. A 1 liter, graduated, stopper top, volumetric cylinder was used with 100 ml of 1% w/w, as is, shampoo solution at room temperature. An axis was fitted at the 600 ml mark, and the cylinder was rotated, by hand, about this axis for 20 half revolutions - first in one direction, followed by return to vertical. The recorded initial foam volume was the total measured foam volume plus liquid volume measured immediately when the 20 half revolutions are completed, minus the volume of liquid that drains from the foam at the point where a stable, observable liquid/foam interface first forms. The final foam volume value was the total foam volume measured after five minutes minus the total liquid that has drained out of the foam during that time. These values reflect the stability of the foam.

#### EXAMPLE 7

Baby shampoo formulations 48-52 were made in accordance with the invention using the ingredients specified in Table 18. Viscosity values for the formulations were determined as in Example 1 and are listed in Table 19.

Ingredients	Table 18				
	48	49	50	51	52
	%	%	%	%	%
Dermothix 75	2.0	-----	-----	-----	-----
Crothix	-----	2.0	-----	-----	-----
Dermothix 100	-----	-----	2.0	-----	-----
PEG 6000 Distearate	-----	-----	-----	2.0	-----
Sodium Laureth(2) Sulfate	15.0	15.0	15.0	15.0	15.0
Miranol C2 M conc. NP	15.0	15.0	15.0	15.0	15.0
Polysorbate 20	15.0	15.0	15.0	15.0	15.0
Water	52.0	52.0	52.0	52.0	54.0
Phenobact	1.0	1.0	1.0	1.0	1.0
	100.0	100.0	100.0	100.0	100.0

Table 19

Viscosity Results:		Initial/Final Foam	
Example#	Viscosity (cps)	Volume (mls)*	Comments
48	350	170/150	Clear liquid
49	525	230/200	Clear liquid
50	50	230/200	Clear liquid
51	50	160/140	Clear liquid
52	12.5	170/150	Clear liquid

The formulations illustrated in this Example show that in a baby shampoo formula, the thickeners are effective at increasing the viscosity, although to varying degrees, and do not have a deleterious effect upon the foam volumes generated by the shampoo.

### EXAMPLE 8

Emulsion formulations 53-57 (Table 20) were prepared in accordance with the invention. These emulsion formulations were thickened with ethoxylated fatty alcohol urethane dimers. Viscosity values for the formulations were determined using a Brookfield LVT viscometer equipped with a heliopath stand and a T-F spindle and are listed in Table 21.

Table 20

Ingredients	53	54	55	56	57
	%	%	%	%	%
Dermothix 75	1.0	----	----	----	----
Crothix	----	1.0	----	----	----
Dermothix 100	----	----	1.0	----	----
PEG 6000 Distearate	----	----	----	1.0	----
Ceteareth 14	1.0	1.0	1.0	1.0	1.0
Cetyl Alcohol	2.0	2.0	2.0	2.0	2.0
Stearyl Alcohol	2.0	2.0	2.0	2.0	2.0
Mineral Oil	15.0	15.0	15.0	15.0	15.0
Water	76.0	76.0	76.0	76.0	77.0
Glycerin	2.0	2.0	2.0	2.0	2.0
Phenobact	1.0	1.0	1.0	1.0	1.0
	100.0	100.0	100.0	100.0	100.0

Table 21

## Viscosity Results:

Formulation	Viscosity (cps)	comments
53	399,000	Thick cream
54	2,028,000	Thick cream
55	1,560,000	Thick cream
56	1,061,000	Thick cream
57	218,000	Very thick lotion (some flow)

The results of the experiments of this Example showed that the thickeners are effective, to differing degrees, at increasing viscosity in the illustrated emulsions. Dermothix 100 was determined to be more effective as an emulsion thickener than Dermothix 75. These results are in contrast to those of the shampoo and single surfactant studies (e.g., Example 1) in which Dermothix 75 was determined to be consistently better than Dermothix 100 at increasing viscosity.

It is to be understood by those skilled in the art that the foregoing descriptions and examples are illustrative of practicing the present invention, but are in no way limiting. Variations of the details presented herein may be made without departing from the spirit and scope of the present invention as defined by the following claims.